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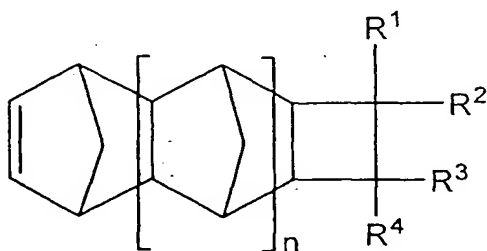
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(54) Title: PHOTORESISTS, FLUOROPOLYMERS AND PROCESSES FOR 157 NM MICROLITHOGRAPHY



(I)

(57) Abstract: The invention provides a polymer having (a) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and (b) at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure: (I) wherein n is 0, 1, or 2; and R<sup>1</sup> to R<sup>4</sup> are independently H; C<sub>1</sub>-C<sub>10</sub> alkyl or alkoxy, optionally substituted by halogen or ether oxygens; or C<sub>6</sub>-C<sub>20</sub> aryl. These polymers can be used in making photoresist compositions and coated substrates.

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## TITLE

Photoresists, Fluoropolymers and Processes for 157 nm Microlithography

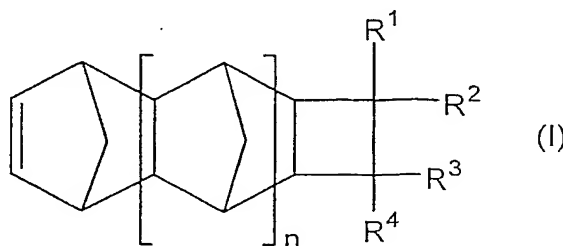
BACKGROUND OF THE INVENTION

The present invention relates to fluorine-containing copolymers derived from at least one fluorinated olefin, at least one polycyclic ethylenically unsaturated polycyclic monomer with a fused 4-membered ring, and, optionally, other components. The polymers are useful for photoimaging compositions and, in particular, photoresist compositions (positive-working and/or negative-working) for imaging in the production of semiconductor devices. The polymers are especially useful in photoresist compositions having high UV transparency (particularly at short wavelengths, e.g., 157 nm) which are useful as base resins in resists and potentially in many other applications.

There is a critical need for resist compositions for use at 193 nm, and particularly at 157 nm, or lower that have not only high transparency at these short wavelengths but also suitable other key properties, including good plasma etch resistance and adhesive properties.

SUMMARY OF THE INVENTION

This invention provides a fluorine-containing copolymer comprising:  
 (a) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and  
 (b) at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure (I):



wherein n is 0, 1, or 2; and

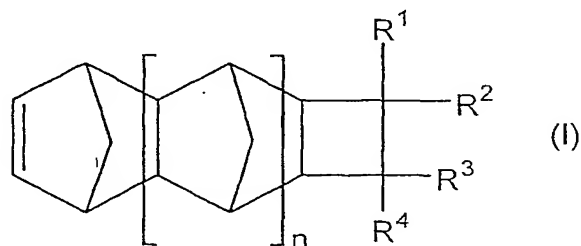
R<sup>1</sup> to R<sup>4</sup> are independently H; C<sub>1</sub> – C<sub>10</sub> alkyl or alkoxy, optionally substituted by halogen or ether oxygens; or C<sub>6</sub> – C<sub>20</sub> aryl.

This invention also provides a photoresist composition comprising:

(a) a fluorine-containing copolymer comprising:

(i) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and

(ii) at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure:



wherein  $n$  is 0, 1, or 2; and

$R^1$  to  $R^4$  are independently H;  $C_1 - C_{10}$  alkyl or alkoxy, optionally substituted by halogen or ether oxygens; or  $C_6 - C_{20}$  aryl; and

(b) a photoactive component.

This invention also provides a coated substrate comprising:

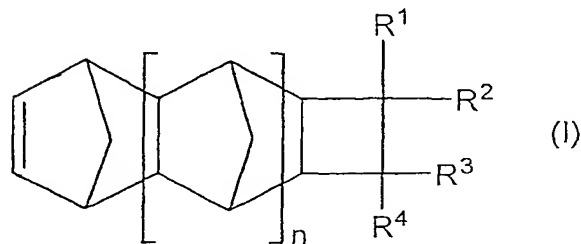
(a) a substrate; and

(b) a photoresist composition comprising a fluorine-containing copolymer comprising:

(i) a fluorine-containing copolymer comprising:

(a') at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and

(b') at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure:

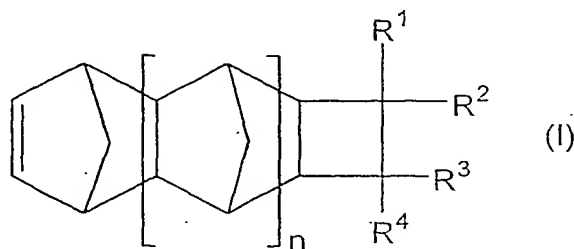


wherein  $n$  is 0, 1, or 2; and  
 $R^1$  to  $R^4$  are independently H;  $C_1 - C_{10}$  alkyl or alkoxy,  
optionally substituted by halogen or ether oxygens; or  
 $C_6 - C_{20}$  aryl; and

(ii) a photoactive component.

#### Fluorinated Copolymers

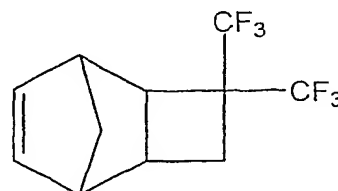
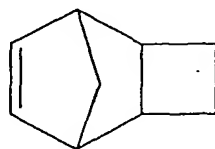
A fluorine-containing copolymer of this invention comprises at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom and at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure (I):



wherein  $n$  is 0, 1, or 2; and  $R^1$  to  $R^4$  are independently H;  $C_1 - C_{10}$  alkyl or alkoxy, optionally substituted by halogen or ether oxygens; or  $C_6 - C_{20}$  aryl.

Preferred compounds of structure (I) are those in which  $n$  is zero.

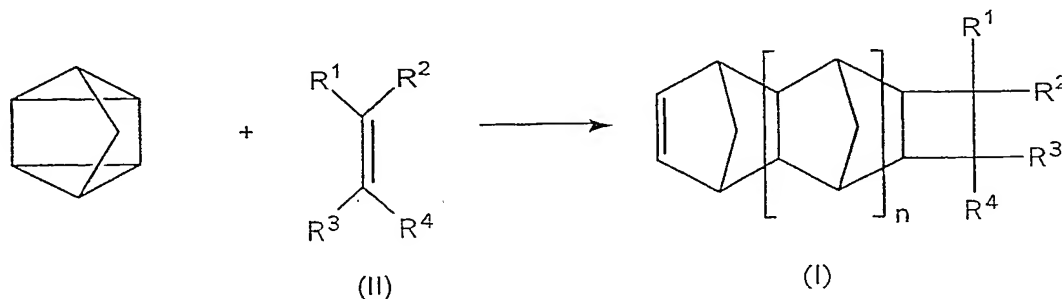
Some illustrative, but nonlimiting, examples of representative monomers of structure (I) and within the scope of the invention are presented below:



Compounds of structure (I) wherein  $n = 0$  may be prepared by methods known in the art such as those disclosed by Sauers et al., *Journal of Organic Chemistry*, Vol. 33, pp. 2175-2181 (1968), or by

DeLucchi et al., *Tetrahedron Letters*, Vol. 25, pp 3642-3646 (1984). One method involves thermal cycloaddition reaction of unsaturated compounds of structure (II) with quadricyclane (tetracyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane) as shown in the equation below and illustrated by the examples.

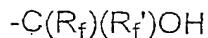
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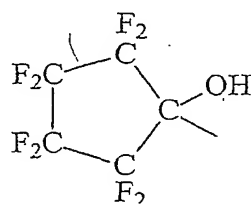
The reaction may be conducted at temperatures ranging from about -50 °C to about 200 °C, more typically from about 0 °C to about 150 °C, in the absence or presence of an inert solvent such as diethyl ether. For reactions conducted at or above the boiling point of one or more of the reagents or solvent, a closed reactor is typically used to avoid loss of volatile components. Compounds of structure (I) where  $n = 1$  or 2, may be prepared by reaction of compounds of structure (I) with  $n = 0$  with cyclopentadiene, as is known in the art.

The fluorine-containing copolymer also comprises a repeat unit derived from at least one ethylenically unsaturated compound (a fluoro-olefin) containing at least one fluorine atom attached to an ethylenically unsaturated carbon. The fluoro-olefin comprises 2 to 20 carbon atoms. Representative fluoro-olefins include, but are not limited to: tetrafluoroethylene; hexafluoropropylene; chlorotrifluoroethylene; vinylidene fluoride; vinyl fluoride; perfluoro-(2,2-dimethyl-1,3-dioxole); perfluoro-(2-methylene-4-methyl-1,3-dioxolane);  $\text{CF}_2=\text{CFO}(\text{CF}_2)_t\text{CF}=\text{CF}_2$ , where  $t$  is 1 or 2; and  $\text{R}_f'\text{OCF}=\text{CF}_2$  wherein  $\text{R}_f''$  is a saturated fluoroalkyl group of from 1 to 10 carbon atoms. A preferred fluoro-olefin is tetrafluoroethylene.

The copolymers of this invention can further comprise structural units derived from one or more additional comonomers. For example, the copolymer of this invention can also comprise a fluoroalcohol group. The fluoroalcohol group can be derived from at least one ethylenically unsaturated compound containing a fluoroalcohol group having the structure:

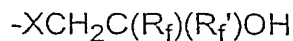


wherein  $\text{R}_f$  and  $\text{R}_f'$  are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together are  $(\text{CF}_2)_m$  wherein  $m$  is 2 to 10.  $\text{R}_f$  and  $\text{R}_f'$  can be partially fluorinated alkyl groups or fully fluorinated alkyl groups (i.e., perfluoroalkyl groups). The term "taken together" indicates that  $\text{R}_f$  and  $\text{R}_f'$  are not separate, discrete fluorinated alkyl groups, but that together they form a ring structure, such as is illustrated below in case of a 5-membered ring:



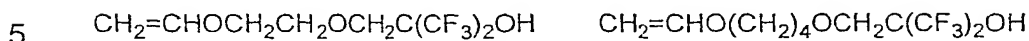
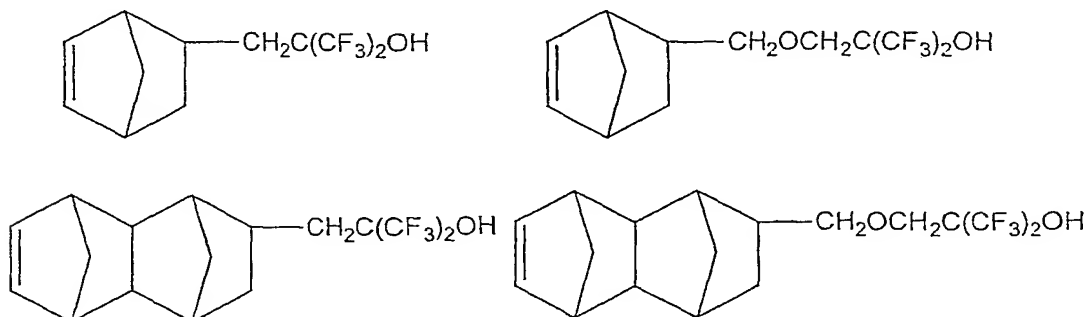
$\text{R}_f$  and  $\text{R}_f'$  can be partially fluorinated alkyl groups without limit according to the invention except that there must be a sufficient degree of fluorination present to impart acidity to the hydroxyl ( $-\text{OH}$ ) of the fluoroalcohol functional group, such that the hydroxyl proton is substantially removed in basic media, such as in aqueous sodium hydroxide solution or tetraalkylammonium hydroxide solution. In preferred cases according to this invention, there will be sufficient fluorine substitution present in the fluorinated alkyl groups of the fluoroalcohol functional group such that the hydroxyl group will have a  $\text{pK}_a$  of 5 - 11. Preferably,  $\text{R}_f$  and  $\text{R}_f'$  are independently perfluoroalkyl group of 1 to 5 carbon atoms; most preferably,  $\text{R}_f$  and  $\text{R}_f'$  are both trifluoromethyl ( $\text{CF}_3$ ).

The fluorinated polymers, photoresists, and processes of this invention that contain a fluoroalcohol functional group can have the structure:

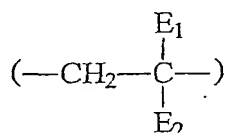


wherein  $\text{R}_f$  and  $\text{R}_f'$  are as described above,  $\text{X}$  is an element from Group VA and VIA of the Periodic Table of the Elements (CAS Version), for example, oxygen, sulfur, nitrogen and phosphorous. Oxygen is the preferred  $\text{X}$  group.

Some illustrative, but nonlimiting, examples of representative comonomers containing a fluoroalcohol functional group and within the scope of the invention are presented below:



10      The copolymer can further comprise an acid-containing or protected acid-containing structural unit:



wherein

- 15       $\text{E}_1$  is H or  $\text{C}_1\text{--C}_{12}$  alkyl;  
 $\text{E}_2$  is  $\text{CO}_2\text{E}_3$ ,  $\text{SO}_3\text{E}$ , or other acidic group; and  
 $\text{E}$  and  $\text{E}_3$  are H or unsubstituted or heteroatom-substituted  $\text{C}_1\text{--C}_{12}$  alkyl.

Suitable heteroatoms are oxygen, nitrogen, sulfur, halogen or phosphorus atoms. When the heteroatom is oxygen, the substituent may  
 20      contain a hydroxyl group. Alkyl groups can contain one to twelve, preferably one to eight, carbon atoms. A preferred acid-containing polymer for aqueous processability (aqueous development) in use, particularly as a binder in a photoresist composition, is a carboxylic acid-



containing copolymer. The level of carboxylic acid groups is typically determined for a given photoresist composition by optimizing the amount needed for good development in aqueous alkaline developer. The additional monomers can be acrylates. Tertiary alkyl acrylates such as  
5 tert-butyl acrylate, 2-methyl-2-adamantyl acrylate and 2-methyl-2-norbornyl acrylate may provide acid sensitive functionality for image formation as discussed above. Other acrylates, such as acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, 2-hydroxyethyl acrylate, 2-methoxyethyl acrylate, 2-cyanoethyl acrylate, glycidyl acrylate and 2,2,2-  
10 trifluoroethyl acrylate can be employed to modify the adhesion or solubility of the polymer especially when used in a photoresist composition. In one embodiment tert-butylacrylate can be incorporated into the polymer, which introduces acid-labile tert-butyl ester groups.

Polar monomers such as vinyl acetate can also be incorporated  
15 into the copolymer in order to assist aqueous development or otherwise modify polymer properties.

The fluoroalcohol group and/or other acid group of the polymer can contain a protecting group that protects the fluorinated alcohol group and/or other acid group (i.e., the protected group) from exhibiting its  
20 acidity while in this protected form. As one illustrative example, the tertiary-butyl group is the protecting group in a tertiary-butyl ester and this protecting group protects the free acid. In undergoing deprotection (conversion of protected acid to free acid), the ester is converted to the corresponding acid.

25 An alpha-alkoxyalkyl ether group is a preferred protecting group for the fluoroalcohol group in order to maintain a high degree of transparency in the photoresist composition. The resulting protected fluoroalcohol group has the structure:



In this protected fluoroalcohol,  $R_f$  and  $R_f'$  are as described above;  $R^8$  is H, a linear  $C_1 - C_{10}$  alkyl group or a branched  $C_3 - C_{10}$  alkyl group. An illustrative, but non-limiting, example of an alpha-alkoxyalkyl ether group  
35 that is effective as a protecting group in a protected acid group is methoxy methyl ether (MOM). A protected fluoroalcohol with this particular

protecting group can be obtained by reaction of chloromethylmethyl ether with the fluoroalcohol.

5 The fluoroalcohol functional group (protected or unprotected) of this invention can be used alone or in combination with one or more other acid groups, such as a carboxylic acid functional group (unprotected) or a t-butyl ester of carboxylic acid functional group (protected).

10 In this invention, often, but not always, the components having protected groups are repeat units having protected acid groups that have been incorporated in the copolymer. Frequently the protected acid groups are present in one or more comonomers that are polymerized to form the copolymer of this invention. Alternatively, in this invention, a copolymer can be formed by copolymerization with an acid-containing comonomer and then subsequently acid functionality in the resulting acid-containing copolymer can be partially or wholly converted by appropriate means to  
15 derivatives having protected acid groups.

The preferred process for polymerizing the fluorine-containing copolymers of this invention is radical addition polymerization. Any suitable polymerization initiator, such as di-(4-tert-butylcyclohexyl)peroxydicarbonate, can be used under appropriate conditions. The  
20 polymerization pressure can range from about 50 to about 10,000 psig, preferably from about 200 to about 1,000 psig. The polymerization temperature can range from about 30°C to about 120°C, preferably from about 40°C to about 80°C. Suitable solvents include 1,1,2-trichlorofluoroethane and non-chlorofluorocarbon solvents such as  
25 1,1,1,3,3-pentafluorobutane. The polymerization process is further enhanced by a semi-batch synthesis. In the semibatch synthesis, a part of the monomer mixture is placed in the reaction vessel and then, portionwise or continuously, the remaining monomers and initiator are added to the vessel throughout the polymerization process.

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#### Photoresist Development

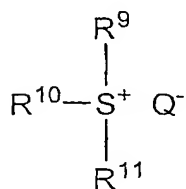
#### Protective Groups for Removal by PAC Catalysis

##### Photoactive Component (PAC)

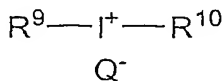
35 The photoresist compositions of this invention contains at least one photoactive component (PAC) that can produce either acid or base upon exposure to actinic radiation during the development process. If an acid is produced upon exposure to actinic radiation, the PAC is termed a

photoacid generator (PAG). If a base is produced upon exposure to actinic radiation, the PAG is termed a photobase generator (PBG).

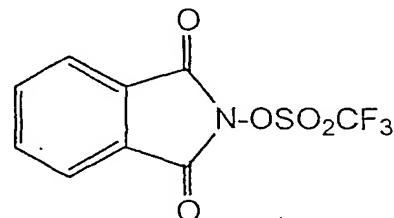
Suitable photoacid generators for this invention include, but are not limited to, 1) sulfonium salts (structure III), 2) iodonium salts (structure IV),  
 5 and 3) hydroxamic acid esters, such as structure V.



III



IV



V

In structures III to IV,  $\text{R}^9$  to  $\text{R}^{11}$  are, independently, substituted or  
 10 unsubstituted  $\text{C}_6 - \text{C}_{20}$  aryl, or substituted or unsubstituted  $\text{C}_7 - \text{C}_{40}$  alkylaryl or aralkyl. Representative aryl groups include, but are not limited to, phenyl, naphthyl, and anthracenyl. Suitable heteroatom substituents include, but are not limited to one or more oxygen, nitrogen, halogen or sulfur atoms. When the heteroatom is oxygen, the substituent may  
 15 contain hydroxyl (-OH) or  $\text{C}_1 - \text{C}_{20}$  alkyloxy (e.g.,  $\text{C}_{10}\text{H}_{21}\text{O}$ ). The anion  $\text{Q}^-$  in structures III - IV can be, but is not limited to,  $\text{SbF}_6^-$  (hexafluoroantimonate),  $\text{CF}_3\text{SO}_3^-$  (trifluoromethylsulfonate = triflate), and  $\text{C}_4\text{F}_9\text{SO}_3^-$  (perfluorobutylsulfonate).

#### Functionality for Development

20 For use in a photoresist composition, the fluorine-containing copolymer should contain sufficient functionality to render the photoresist developable so as to produce a relief image, following imagewise exposure to ultraviolet radiation having wavelength of  $\leq 365$  nm. In some preferred embodiments, the sufficient functionality is selected from an acid  
 25 and/or a protected acid group, as described above. Such acid or protected acid groups have been found to render the exposed portions of photoresist soluble in basic solution upon exposure to sufficient ultraviolet radiation having a wavelength of  $\leq 365$  nm while the unexposed portions are insoluble in the basic solution.

30 For development, one or more groups within the fluorine-containing copolymers should contain one or more components having protected acid groups that can yield, by catalysis of acids or bases generated

photolytically from the photoactive compound (PAC), hydrophilic acid or base groups.

5 A given protected acid group is one that is normally chosen on the basis of its being acid labile, such that when photoacid is produced upon imagewise exposure, the acid will catalyze deprotection and production of hydrophilic acid groups that are necessary for development under aqueous conditions. In addition, the fluorine-containing copolymers may also contain acid functionality that is not protected.

10 Examples of basic developer include but are not limited to sodium hydroxide solution, potassium hydroxide solution, and ammonium hydroxide solution. Specifically a basic developer is an aqueous alkaline liquid such as a wholly aqueous solution containing 0.262 N tetramethylammonium hydroxide (with development at 25 °C usually  $\leq 2$  min) or 1 % sodium carbonate by weight (with development at a  
15 temperature of 30 °C usually  $\leq 2$  minutes).

When an aqueous processable photoresist is coated or otherwise applied to a substrate and imagewise exposed to UV light, development of the photoresist composition may require that the binder material contain sufficient acid groups (e.g., carboxylic acid groups) and/or protected acid  
20 groups that are at least partially deprotected upon exposure to render the photoresist (or other photoimageable coating composition) processable in aqueous alkaline developer.

In one embodiment of the invention the copolymer having one or more protected acid groups yields a carboxylic acid as the hydrophilic  
25 group upon exposure to photogenerated acid. Such protected acid groups include, but are not limited to, A) esters capable of forming, or rearranging to, a tertiary cation, B) esters of lactone, C) acetal esters, D)  $\beta$ -cyclic ketone esters, E)  $\alpha$ -cyclic ether esters, and F) MEEMA (methoxy ethoxy ethyl methacrylate) and other esters which are easily  
30 hydrolyzable because of anchimeric assistance. Some specific examples in category A) are t-butyl ester, 2-methyl-2-adamantyl ester, and isobornyl ester.

A typical acidic group is the hexafluoroisopropanol group which can be incorporated by use of hexafluoroisopropanol-containing monomers.  
35 Some or all of the hexafluoroisopropanol groups may be protected as, for example, acid-labile alkoxymethyl ethers or tert-butylcarbonates.

Examples of components having protected acid groups that yield an alcohol as the hydrophilic group upon exposure to photogenerated acid

or base include, but are not limited to, t-butoxycarbonyl (t-BOC), t-butyl ether, and 3-cyclohexenyl ether.

In the case of a negative-working photoresist layer, the photoresist layer will be removed during development in portions which are unexposed to UV radiation but will be substantially unaffected in exposed portions during development using either a critical fluid or an organic solvent.

#### Dissolution Inhibitors and Additives

Various dissolution inhibitors can be utilized in this invention. Ideally, dissolution inhibitors (DIs) for far and extreme UV resists (e.g., 193 nm resists) should be designed and/or chosen to satisfy multiple materials needs, including dissolution inhibition, plasma etch resistance, and adhesion behavior of resist compositions comprising a given DI additive. Some dissolution inhibiting compounds also serve as plasticizers in resist compositions.

A variety of bile-salt esters (i.e., cholate esters) are particularly useful as DIs in the compositions of this invention. Bile-salt esters are known to be effective dissolution inhibitors for deep UV resists, beginning with work by Reichmanis et al. in 1983. (E. Reichmanis et al., "The Effect of Substituents on the Photosensitivity of 2-Nitrobenzyl Ester Deep UV Resists", *J. Electrochem. Soc.* 1983, 130, 1433-1437.) Bile-salt esters are particularly attractive choices as DIs for several reasons, including their availability from natural sources, their high alicyclic carbon content, and particularly for their transparency in the deep and vacuum UV region (which essentially is also the far and extreme UV region) of the electromagnetic spectrum. Typically, they are highly transparent at 193 nm. Furthermore, the bile-salt esters are attractive DI choices since they may be designed to have widely ranging hydrophobic to hydrophilic compatibilities, depending upon hydroxyl substitution and functionalization.

Representative bile-acids and bile-acid derivatives that are suitable as additives and/or dissolution inhibitors for this invention include, but are not limited to, cholic acid, deoxycholic acid, lithocholic acid, t-butyl deoxycholate, t-butyl lithocholate, and t-butyl-3- $\alpha$ -acetyl lithocholate.

The invention is not limited to use of bile-acid esters and related compounds as dissolution inhibitors. Other types of dissolution inhibitors, such as various diazonaphthoquinones (DNQs) and diazocoumarins (DCs), can be utilized in this invention in some

applications. Diazanaphthoquinones and diazocoumarins are generally suitable in resists compositions designed for imaging at higher wavelengths of UV light (e.g., 365 nm and perhaps at 248 nm). These dissolution inhibitors are generally not preferred in resist compositions designed for imaging with UV light at 193 nm or lower wavelengths, since these compounds absorb strongly in this region of the UV and are usually not sufficiently transparent for most applications at these low UV wavelengths.

#### Solvents:

Photoresists of this invention are prepared as coating compositions by dissolving the components of the photoresist in a suitable solvent, for example, ether esters such as propyleneglycol monomethyl ether acetate, 2-ethoxyethyl acetate, 2-methoxyethyl acetate, and ethyl 3-ethoxypropionate; ketones such as cyclohexanone, 2-heptanone, and methyl ethyl ketone; esters such as butyl acetate, ethyl lactate, methyl lactate, and ethyl acetate; glycol ethers such as propylene glycol monomethyl ether, ethylene glycol monomethyl ether, ethyleneglycol monoethyl ether, and 2-methoxyethyl ether (diglyme); unsubstituted and substituted hydrocarbons and aromatic hydrocarbons such as hexane, toluene, and chlorobenzene; or fluorinated solvents such as CFC-113 (1,1,2-trichlorotrifluoromethane, E. I. du Pont de Nemours and Company), and 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane. High boiling solvents can be added such as xylene or other unsubstituted or substituted aromatic hydrocarbons; ethers such as benzyl ethyl ether, and dihexyl ether; glycol ethers such as diethyleneglycol monomethyl ether, and diethyleneglycol monoethyl ether; ketones such as acetonylacetone and isophorone; alcohols such as 1-octanol, 1-nonanol, and benzylalcohol; esters such as benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, ethylene carbonate, and propylene carbonate; or lactones such as  $\gamma$ -butyrolactone, and  $\delta$ -valerolactone. Alternatively, supercritical CO<sub>2</sub> may be useful as a solvent. These solvents can be used alone or in admixture of two or more. Typically, the solids content of the photoresist varies between 5% and 50% by weight of the total weight of the photoresist composition.

#### Other Components

The compositions of this invention can contain optional additional components. Examples of additional components which can be added include, but are not limited to, bases, surfactants, resolution enhancers,

adhesion promoters, residue reducers, coating aids, plasticizers, and  $T_g$  (glass transition temperature) modifiers.

#### Process Steps

For microlithography, the photoresist composition is applied to a  
5 suitable substrate such as a microelectronic wafer typically employed in the semiconductor industry. The solvent is then removed by evaporation.

#### Imagewise Exposure

The photoresist compositions of this invention are sensitive in the ultraviolet region of the electromagnetic spectrum and especially to those  
10 wavelengths  $\leq 365$  nm. The photoresist compositions of this invention can be imagewise exposed at many different UV wavelengths including, but not limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise exposure is preferably done with ultraviolet light of 248 nm, 193 nm, 157 nm, or lower wavelengths; is more preferably done with  
15 ultraviolet light of 193 nm, 157 nm, or lower wavelengths; and is still more preferably done with ultraviolet light of 157 nm or lower wavelengths. Imagewise exposure can either be done digitally with a laser or equivalent device or non-digitally with use of a photomask. Digital imaging with a laser is preferred. Suitable laser devices for digital imaging of the  
20 compositions of this invention include, but are not limited to, argon-fluorine excimer lasers with UV output at 193 nm, krypton-fluorine excimer lasers with UV output at 248 nm, and fluorine (F2) lasers with output at 157 nm. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution  
25 limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g., 248 nm or higher). Specifically, imaging at 157 nm is preferred over imaging at 193 nm.

The photoresists of this invention are useful for 365 nm (I-line),  
30 248 nm (KrF laser), and especially 193 nm (ArF laser) and 157 nm (F2 laser) microlithography. For imaging at 193 and 157 nm, it is preferred that the polymer is substantially free of aromatic groups because these absorb significant amounts of light at these wavelengths. These photoresists are critical in allowing for the imaging of feature sizes in the  
35 submicron range.

#### Substrate

The substrate employed in this invention is typically a microelectronic wafer and can be silicon, silicon oxide, silicon oxynitride,

silicon nitride, or various other materials used in semiconductive manufacture. Typically, the microelectronic wafer is prepared from silicon, silicon oxide, silicon oxynitride and silicon nitride.

5

GLOSSARYAnalytical/Measurements

	bs	broad singlet
	$\delta$	NMR chemical shift measured in the indicated solvent
10	g	gram
	h	hours
	NMR	Nuclear Magnetic Resonance
	$^1\text{H}$ NMR	Proton NMR
	$^{13}\text{C}$ NMR	Carbon-13 NMR
15	$^{19}\text{F}$ NMR	Fluorine-19 NMR
	s	singlet
	sec.	second(s)
	m	multiplet
	mL	milliliter(s)
20	mm	millimeter(s)
	$T_g$	Glass Transition Temperature
	$M_n$	Number-average molecular weight of a given polymer
	$M_w$	Weight-average molecular weight of a given polymer
25	$P = M_w/M_n$	Polydispersity of a given polymer
	Absorption coefficient	$AC = A/b$ , where A, absorbance, $= \log_{10}(1/T)$ and b = film thickness in microns, where T = transmittance as defined below.
30	Transmittance	Transmittance, T, = ratio of the radiant power transmitted by a sample to the radiant power incident on the sample and is measured for a specified wavelength $\lambda$ (e.g., nm).
35		

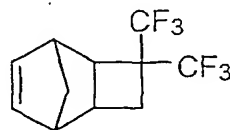
Chemicals/Monomers

Perkadox® 16 N

Di-(4-tert-butylcyclohexyl)peroxydicarbonate  
Noury Chemical Corp., Burt, NY



Solkane® 365 mfc 1,1,1,3,3-Pentafluorobutane  
Solvay Fluor, Hannover, Germany



5 TCN-(CF<sub>3</sub>)<sub>2</sub>  
TFE

Tetrafluoroethylene  
E. I. du Pont de Nemours and Company,  
Wilmington, DE

THF

Tetrahydrofuran  
Aldrich Chemical Co., Milwaukee, WI

10 Ultraviolet

Extreme UV

Region of the electromagnetic spectrum in  
the ultraviolet that ranges from  
10 nanometers to 200 nanometers

Far UV

15

Region of the electromagnetic spectrum in  
the ultraviolet that ranges from  
200 nanometers to 300 nanometers

UV

Ultraviolet region of the electromagnetic  
spectrum which ranges from 10 nanometers  
to 390 nanometers

20

Near UV

Region of the electromagnetic spectrum in  
the ultraviolet that ranges from  
300 nanometers to 390 nanometers

### EXAMPLES

25 Unless otherwise specified, all temperatures are in degrees  
Celsius, all mass measurements are in grams, and all percentages are  
weight percentages, except for polymer compositions, which are  
expressed as mole % of the constituent monomer repeat units.

30 Glass transition temperatures ( $T_g$ ) were determined by DSC  
(differential scanning calorimetry) using a heating rate of 20 °C/min; data  
is reported from the second heat. The DSC unit used is a Model  
DSC2910 made by TA Instruments, Wilmington, DE.

35 Assessment of 157 nm imaging sensitivity can be done using a  
Lambda-Physik Compex 102 excimer laser configured for 157 nm  
operation. Vacuum ultraviolet transmission measurements are made  
using a McPherson spectrometer equipped with a D2 light source.

Samples are spin-coated at several thicknesses on  $\text{CaF}_2$  substrates, and the contribution of the substrate to the transmission is approximately removed by spectral division.

More specifically, all absorption coefficient measurements for  
5 polymers can be made using the procedure listed below.

1. Samples are first spin-coated on silicon wafers on a Brewer Cee (Rolla, MO), Spincoater/Hotplate model 100CB.

a) Two to four silicon wafers are spun at different speeds  
(e.g., 2000, 3000, 4000, 6000 rpm) to obtain differing film thickness and  
10 the coated wafers are subsequently baked at 120 °C for 30 min. The dried films are then measured for thickness on a Gaertner Scientific (Chicago, IL), L116A Ellipsometer (400 to 1200 angstrom range). Two spin speeds are then selected from this data to spin the  $\text{CaF}_2$  substrates for the spectrometer measurement.

b) Two  $\text{CaF}_2$  substrates (1" dia. x 0.80" thick) are selected  
15 and each is run as a reference data file on a McPherson Spectrometer (Chemsford, MA), 234/302 monochromator, using a 632 Deuterium Source, 658 photomultiplier, and Keithley 485 picoammeter.

c) Two speeds are selected from the silicon wafer data a) to  
20 spin the sample material onto the  $\text{CaF}_2$  reference substrates (e.g., 2000 and 4000 rpm) to achieve the desired film thickness. Then each is baked at 120 °C for 30 min. and the sample spectra is collected on the McPherson Spectrometer; the sample files are then divided by the reference  $\text{CaF}_2$  files.

d) The resulting absorbance files are then adjusted (sample  
25 film on  $\text{CaF}_2$  divided by  $\text{CaF}_2$  blank) for film thickness to give absorbance per micron (abs/mic), which is done using GRAMS386 and KALEIDAGRAPH software.

The term "clearing dose" indicates the minimum exposure energy  
30 density (e.g., in units of  $\text{mJ}/\text{cm}^2$ ) to enable a given photoresist film, following exposure, to undergo development.

#### Example 1.

##### Preparation of TCN-(CF<sub>3</sub>)<sub>2</sub>.

A 400 mL Hastelloy shaker tube was charged with 35 g of  
35 quadricyclane (0.3 mol calculated for 80% purity quadricyclane, sample contained 15 % ether and 5 % norbornadiene) and 50 g (0.3 mol) of 3,3,3-trifluoro-2-(trifluoromethyl)propene and kept at 120 °C for 16 h. The

reactor was vented, unloaded and crude product (58 g) was distilled under vacuum to give 41 g of TCN-(CF<sub>3</sub>)<sub>2</sub>; b.p. 72-73 °C /44 mm.

<sup>19</sup>F NMR (CDCl<sub>3</sub>): -66.18 (3F, q; 10.3Hz), -74.30(3F, q; 10.3Hz); <sup>1</sup>H

NMR: 1.40(1H), 1.8-2.4(5H, m), 2.87(1H), 3.07(1H), 6.03(1H, m), 6.13 (1H,

5 m); Found: C, 51.29%; H, 3.88%; F, 43.86%.

### Example 2

#### Synthesis of a TFE, TCN-(CF<sub>3</sub>)<sub>2</sub> Polymer

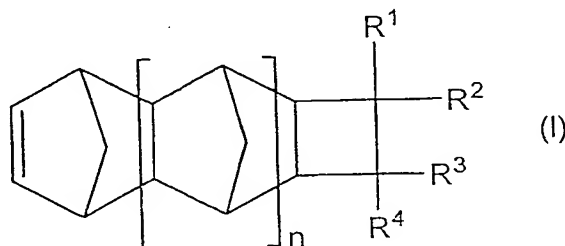
A 200 mL stainless steel pressure vessel was charged with 51.2 g  
10 TCN-(CF<sub>3</sub>)<sub>2</sub>, 50 mL of Solkane® 365 mfc and 1.6 g of Perkadox® 16N  
initiator. The vessel was closed, cooled in dry ice, purged with nitrogen,  
evacuated, and charged with 30 g of TFE. The vessel was then agitated  
with its contents at 50 °C for 18 hr while the internal pressure decreased  
from 241 to 221 psi. The vessel was cooled to room temperature and  
15 vented to 1 atmosphere. The vessel contents were removed using  
additional Solkane® 365 mfc to rinse. This solution was added to excess  
hexane (30-35 mL portion to 650 mL hexane). The precipitated polymer  
was washed with hexane, air-dried for several hours and then dried  
overnight in a vacuum oven with slight nitrogen purge at 88-90 °C. There  
20 was isolated 16.4 g of white polymer; GPC analysis: M<sub>n</sub> 5700, M<sub>w</sub> 7800.  
T<sub>g</sub> 203 °C (DSC). Anal. Found: C, 45.85; H, 3.00; F, 49.26. <sup>19</sup>F NMR (δ,  
THF-d<sub>8</sub>) -67 (3 F from TCN-(CF<sub>3</sub>)<sub>2</sub>), -76 (3 F from TCN-(CF<sub>3</sub>)<sub>2</sub>), -95 to  
-125 (4F from TFE).

# CLAIMS

What is claimed is:

1. A fluorine-containing copolymer comprising:

- (a) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and
- (b) at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure (I):



wherein  $n$  is 0, 1, or 2; and

$R^1$  to  $R^4$  are independently H;  $C_1 - C_{10}$  alkyl or alkoxy,

optionally substituted by halogen or ether oxygens; or  $C_6 - C_{20}$  aryl.

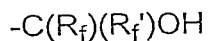
2. The copolymer of Claim 1, wherein (a) is derived from a fluoro-olefin comprising 2 to 20 carbon atoms.

3. The copolymer of Claim 2, wherein the fluoro-olefin is selected from the group consisting of tetrafluoroethylene; hexafluoropropylene; chlorotrifluoroethylene; vinylidene fluoride; vinyl fluoride; perfluoro-(2,2-dimethyl-1,3-dioxole); perfluoro-(2-methylene-4-methyl-1,3-dioxolane);  $CF_2=CFO(CF_2)_tCF=CF_2$ , wherein  $t$  is 1 or 2; and  $R_f''OCF=CF_2$  wherein  $R_f''$  is a saturated fluoroalkyl group of from 1 to 10 carbon atoms.

4. The copolymer of Claim 3, wherein the fluoro-olefin is tetrafluoroethylene.

5. The copolymer of Claim 1, further comprising a fluoroalcohol group or a protected fluoroalcohol group.

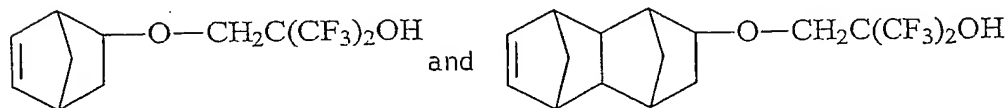
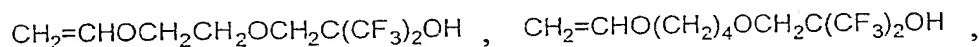
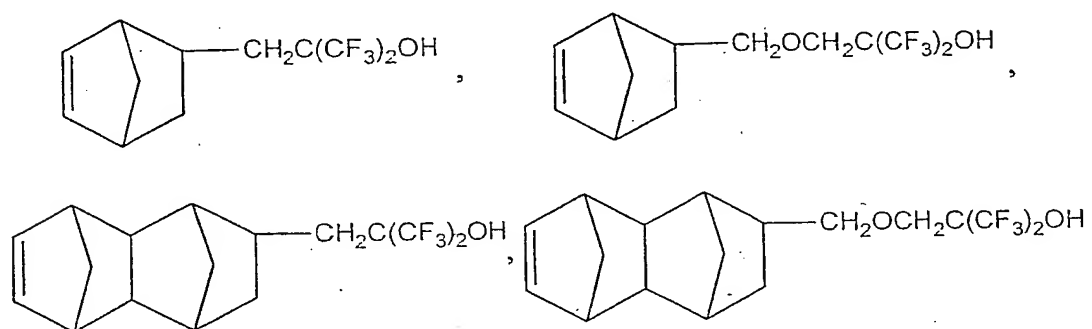
6. The copolymer of Claim 5, wherein the fluoroalcohol group or the protected fluoroalcohol group is derived from at least one ethylenically unsaturated compound containing a fluoroalcohol group having the structure:



wherein  $R_f$  and  $R_f'$  are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together are  $(CF_2)_m$  wherein  $m$  is 2 to 10.

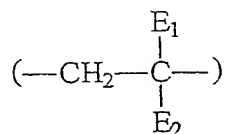
5 7. The copolymer of Claim 6, wherein  $R_f$  and  $R_f'$  are perfluoroalkyl groups.

8. The copolymer of Claim 6, wherein the ethylenically  
unsaturated compound containing the fluoroalcohol group or the protected  
fluoroalcohol group is derived from a monomer selected from the group  
10 consisting of:



15

9. The copolymer of Claim 5, further comprising at least one acid-containing or protected acid-containing structural unit:



wherein E<sub>1</sub> is H or C<sub>1</sub>-C<sub>12</sub> alkyl; E<sub>2</sub> is CO<sub>2</sub>E<sub>3</sub>, SO<sub>3</sub>E, or other acidic group; and E and E<sub>3</sub> are H or unsubstituted or heteroatom-substituted C<sub>1</sub>-C<sub>12</sub> alkyl.

10. The copolymer of Claim 9, wherein the heteroatom is selected from the group consisting of oxygen, nitrogen, sulfur, halogen and phosphorus.

11. The copolymer of Claim 10, wherein the heteroatom is oxygen, and the substituent further contains a hydroxyl group.

12. The copolymer of Claim 9, wherein the acid-containing or protected acid-containing structural unit comprises a carboxylic acid group.

13. The copolymer of Claim 9, wherein the acid-containing or protected acid-containing structural unit is derived from a monomer selected from the group consisting of tert-butyl acrylate; 2-methyl-2-adamantyl acrylate; 2-methyl-2-norbornyl acrylate; acrylic acid; methyl acrylate; ethyl acrylate; propyl acrylate; 2-hydroxyethyl acrylate; 2-methoxyethyl acrylate; 2-cyanoethyl acrylate; glycidyl acrylate and 2,2,2-trifluoroethyl acrylate.

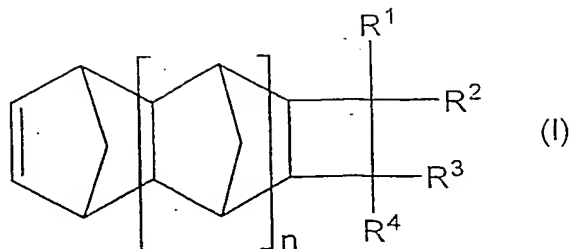
14. The copolymer of Claim 1, further comprising at least one group derived from a polar monomer.

15. A photoresist composition comprising:

(a) a fluorine-containing copolymer comprising:

(i) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and

(ii) at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure:



wherein  $n$  is 0, 1, or 2; and

$R^1$  to  $R^4$  are independently H;  $C_1 - C_{10}$  alkyl or alkoxy,

- 5 optionally substituted by halogen or ether oxygens; or  $C_6 - C_{20}$  aryl; and  
 (b) a photoactive component.

16. The photoresist composition of Claim 15, wherein (i) is derived from a fluoro-olefin comprising 2 to 20 carbon atoms.

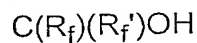
17. The photoresist composition of Claim 16, wherein the fluoro-  
 10 olefin is selected from the group consisting of tetrafluoroethylene; hexafluoropropylene; chlorotrifluoroethylene; vinylidene fluoride; vinyl fluoride; perfluoro-(2,2-dimethyl-1,3-dioxole); perfluoro-(2-methylene-4-methyl-1,3-dioxolane);  $CF_2=CFO(CF_2)_tCF=CF_2$ , wherein  $t$  is 1 or 2; and  $R_f''OCF=CF_2$  wherein  $R_f''$  is a saturated fluoroalkyl group of from 1 to 10  
 15 carbon atoms.

18. The photoresist composition of Claim 17, wherein the fluoro-olefin is tetrafluoroethylene.

19. The photoresist composition of Claim 15, wherein the fluorine-containing copolymer further comprises a fluoroalcohol group or a  
 20 protected fluoroalcohol group.

20. The photoresist composition of Claim 19, wherein the fluoroalcohol or protected fluoroalcohol group is derived from at least one ethylenically unsaturated compound containing a fluoroalcohol group having the structure:

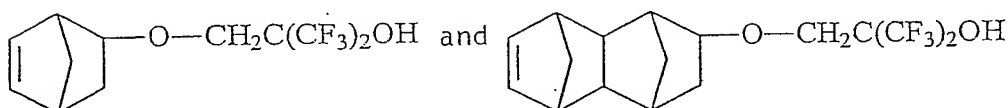
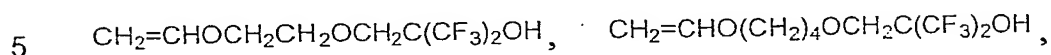
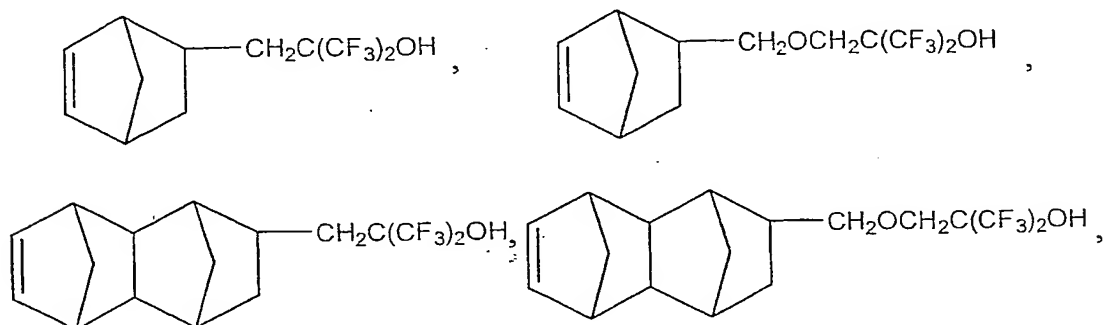
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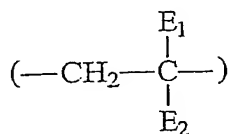
- wherein  $R_f$  and  $R_f'$  are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together are  $(CF_2)_n$  wherein  $n$  is 2  
 30 to 10.

21. The photoresist composition of Claim 20, wherein  $R_f$  and  $R_f'$  are perfluoroalkyl groups.

22. The photoresist composition of Claim 20, wherein the fluoroalcohol group or the protected fluoroalcohol group is derived from a monomer selected from the group consisting of:



10 23. The photoresist composition of Claim 15, wherein the fluorine-containing copolymer further comprises at least one acid-containing or protected acid-containing structural unit:



15

wherein  $\text{E}_1$  is H or  $\text{C}_1\text{--C}_{12}$  alkyl;  $\text{E}_2$  is  $\text{CO}_2\text{E}_3$ ,  $\text{SO}_3\text{E}$ , or other acidic group; and E and  $\text{E}_3$  are H or unsubstituted or heteroatom substituted  $\text{C}_1\text{--C}_{12}$  alkyl.



24. The photoresist composition of Claim 23, wherein the heteroatom is selected from the group of oxygen, nitrogen, sulfur, halogen and phosphorus.

25. The photoresist composition of Claim 24, wherein the heteroatom is oxygen, and the substituent further contains a hydroxyl group.

26. The photoresist composition of Claim 23, wherein the acid-containing or protected acid-containing structural unit comprises a carboxylic acid group.

27. The photoresist composition of Claim 26, wherein the acid-containing or protected acid-containing structural unit is derived from a monomer selected from the group consisting of tert-butyl acrylate; 2-methyl-2-adamantyl acrylate; 2-methyl-2-norbornyl acrylate; acrylic acid; methyl acrylate; ethyl acrylate; propyl acrylate; 2-hydroxyethyl acrylate; 2-methoxyethyl acrylate; 2-cyanoethyl acrylate; glycidyl acrylate and 2,2,2-trifluoroethyl acrylate.

28. The photoresist composition of Claim 15, wherein the fluorine-containing copolymer further comprises at least one group derived from a polar monomer.

29. The photoresist composition of Claim 15, wherein the photoactive component is a photoacid generator.

30. The photoresist composition of Claim 15, further comprising a dissolution inhibitor.

31. The photoresist composition of Claim 15, further comprising a solvent.

32. The photoresist composition of Claim 31, wherein the solvent is selected from the group of ether esters; ketones; esters; glycol ethers; unsubstituted or substituted hydrocarbons; aromatic hydrocarbons; fluorinated solvents and supercritical CO<sub>2</sub>.

33. The photoresist composition of Claim 15, further comprising an additive selected from the group consisting of bases, surfactants, resolution enhancers, adhesion promoters, residue reducers, coating aids, plasticizers, and T<sub>g</sub> (glass transition temperature) modifiers.

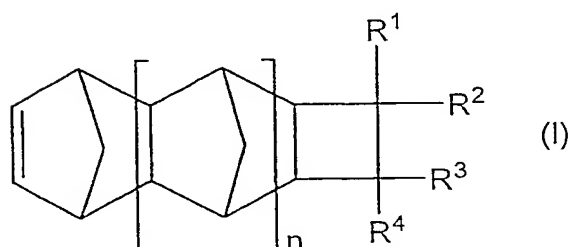
34. A coated substrate comprising:

(a) a substrate; and

(b) a photoresist composition comprising a fluorine-containing copolymer comprising:

(i) a fluorine-containing copolymer comprising:

(a') at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and  
 (b') at least one repeat unit derived from an ethylenically unsaturated cyclic compound of structure:



wherein  $n$  is 0, 1, or 2; and  
 $R^1$  to  $R^4$  are independently H;  $C_1 - C_{10}$  alkyl or alkoxy, optionally substituted by halogen or ether oxygens; or  $C_6 - C_{20}$  aryl; and  
 (ii) a photoactive component.

35. The coated substrate of Claim 34, wherein the substrate is a microelectronic wafer.

36. The coated substrate of Claim 35, wherein the microelectronic wafer comprises a material selected from the group consisting of silicon, silicon oxide, silicon oxynitride, and silicon nitride.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/25023

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : COSF 14/18; G03C 1/73

US CL : 526/250; 430/270.1

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/250; 430/270.1; 526/247; 526/255; 430/325; 430/326; 430/907; 430/331; 430/914

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
USPAT, USPG-PUB, EPO, JPO, DERWENT

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,229,473 (KOBO et al) 20 July 1993 (20.07.1993), abstract, line 1-40; column 1, line 65 - column 2, line 60; column 2, line 50-60; column 6, line 42 - column 7, line 12; column 8, line 46-58. Claims 1-4.	1-4
Y	US 2,928,865 (BRASEN) 15 March 1960 (15.03.1965), column 2, line 21-70; column 9, line 19-28 and 46-54.	1-36
Y	US 2002/0119398 A1 (DESIMONE et al) 29 August 2002 (29.08.2002), paragraphs 0101-0115 and 0087-0096. Claims 5-36	5-36

*We use hydroxy adenosine  
no adenosine (we used)*

*Just 1  
hydroxy  
adenosine  
just 1*

*Kobo requires transcribed rly*

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

08 December 2003 (08.12.2003)

Date of mailing of the international search report

23 JAN 2004

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